CALCULATION OF PERTURBATIONS IN CERTAIN MOLECULAR ELECTRONIC TERMS. PART I. $^2\Sigma - {}^4\Pi$

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ABSTRACT. In this paper expressions are derived for the course of energy levels at the point of intersection of two mutually perturbing molecular electronic states. The method of treatment is given in detail and applied to the perturbation $^2\Sigma - {}^4\Pi$.

INTRODUCTION

Calculation of perturbations has been carried out by a number of investigators previously for the cases of perturbations between singlet-singlet, singlet-triplet, triplet-triplet and doublet-doublet terms. The method employed by these investigators, chief of whom are Ittmann (1931), Budö and Kovács (1938, 1939) is invariably the wave mechanical treatment given by Krönig (1928) and Van Vleck (1929). Budö and Kovács (1939) have extended this work for higher multiplicity terms in their calculation for the perturbation of a $^4\Sigma$ term by a second $^4\Sigma$ term.

In this series of papers the writer proposes to present the results of perturbation calculations for certain electronic terms such as $^2\Sigma - {}^4\Pi$, $^2\Pi - {}^4\Sigma$, $^2\Pi - {}^4\Pi$, $^4\Sigma - {}^4\Pi$, $^4\Pi - {}^4\Pi$ and between those of higher multiplicity like quintets, sextets etc. The importance of these calculations arises on account of the possibility of detecting such terms in the band spectra of the halides and oxides of the heavier elements, Yt, Ta, Cr, Mn, etc. which are under investigation by the author and others in this laboratory.

THEORY

The wave mechanical treatment of the diatomic molecule was given simultaneously by Van Vleck and Krönig. The wave-function ψ of a diatomic molecule with moving nuclei is given by the equation

$$H_0 - \frac{h^2}{8\pi^2 M r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \operatorname{cosec}^2\theta\frac{\partial^2}{\partial\omega^2}\right\} - W\Big|\psi = 0 \quad \ldots \quad (1)$$

where H_0 is the Hamiltonian of a stationary molecule and the other symbols have their usual significance. This equation cannot be readily solved as it is, but if certain small terms are neglected it can be split up into the product of three functions ϕ, R and u, of which ϕ is the solution of the wave equation for a stationary diatomic molecule, R is the wave-function satisfying

the equation of vibration of the nuclei while u is the wave-function satisfying the equation of a symmetric top. The neglected terms are

$$\frac{h^2 i}{8\pi^2 M r^2}\left[\cot\theta(P_x - iP_y P_z - iP_z P_y) + 2\,\mathrm{cosec}\theta P_y \frac{\partial}{\partial\omega} + 2P_x\frac{\partial}{\partial\theta}\right]\psi \qquad (2)$$

and the high frequency part of the expression

$$\frac{h^2}{8\pi^2 M r^2}\left[(P_x^2 + P_y^2)\phi' - 2r\frac{\partial\phi'}{\partial r} - r^2\frac{\partial^2\phi'}{\partial r^2} - \frac{2r^2}{R}\frac{\partial R'}{\partial r}\cdot\frac{\partial\phi'}{\partial r}\right] Ru \qquad (3)$$

The neglected parts can now be taken into consideration by means of a perturbation calculation, treating the electronic wave-functions ϕ as the unperturbed functions. The different types of the finer interaction terms when taken as the perturbing terms give rise to the different correction terms like Λ-doubling, spin-splitting in Σ states etc. The same procedure can also be applied for the case of the irregular perturbations occasioned by the accidental crossing or the very near approach of two unperturbed wave-functions.

Van Vleck, in his work referred to above, has given expressions for the matrix elements of the total Hamiltonian formed with the unperturbed eigenfunctions ϕ. They are

$$\left.\begin{aligned}
&H^\circ(n, v, \Lambda, \Sigma\,;\, n, v, \Lambda, \Sigma \pm 1) = B[J(J+1) - \Omega(\Omega \pm 1)]^{1/2} \\
&\qquad\qquad [S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2} \\
&H^\circ(n, v, \Lambda, \Sigma\,;\, n, v, \Lambda \pm 1, \Sigma) = 2(BL_y)(n, v, \Lambda\,;\, n, v, \Lambda \pm 1) \\
&\qquad\qquad [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} \\
&H^\circ(n, v, \Lambda, \Sigma\,;\, n, v, \Lambda \pm 1, \Sigma \mp 1) = (AL_y + 2BL_y)(n, v, \Lambda\,;\, n, v, \Lambda \\
&\qquad\qquad \pm 1)[S(S+1) - \Sigma(\Sigma \mp 1)]^{1/2} \\
&H^\circ(n, v, \Lambda, \Sigma\,;\, n', v', \Lambda, \Sigma) = C(n, v, \Lambda\,;\, n', v', \Lambda)
\end{aligned}\right\} \quad \ldots \quad (4)$$

Here $n \neq n'$, while the diagonal terms W° are given, by

$$C(n, v, \Lambda\,;\, n, v, \Lambda) + A(n, v, \Lambda\,;\, n, v, \Lambda)\Lambda\Sigma + B[J(J+1) - \Omega^2 + S(S+1) - \Sigma^2] \quad \ldots \quad (5)$$

where in case of Σ states the factor (Kramer's spin-spin interaction term) $\epsilon[3\Sigma^2 - S(S+1)]$ is also to be added. The rest of the matrix elements vanish. In all these matrix elements the phase factors are omitted as, for the purpose of the calculations presented in this paper, only the squares of the absolute values of these matrix elements (*i.e.*, $H_{ik}H_{ik}^* = |H_{ik}|^2$) are necessary. However, it is to be remembered that

$$\left.\begin{aligned}
&L_y(\Pi, \Sigma) = (-1)^{\Sigma} L_y(-\Pi, \Sigma) \text{ and} \\
&L_y(\Lambda, \Lambda') = L_y(-\Lambda, -\Lambda') \text{ for } \Lambda, \Lambda' \neq 0
\end{aligned}\right\} \qquad (6)$$

where the Σ in the exponent is even or odd according as the Σ state under consideration is positive or negative.

It can be seen from the above matrix elements that they connect terms with $\Delta\Omega = 0, \pm 1$ and $\Delta\Lambda = 0, \pm 1$ and there are no matrix elements between

terms of different multiplicities. Hence the observed perturbations between terms of different multiplicities cannot be explained by this means. This is because in the above calculations the interaction between the orbital and spin moments of the individual electrons [which is given by $\Sigma a_i(\vec{l}_i\vec{s}_i)$] is neglected. If this interaction is taken into consideration, it will not only alter the energies (*i.e.*, the diagonal terms) by the small amount $A \wedge \Sigma$, but also change the unperturbed wave-functions slightly so that the new wave-functions are linear combinations of the old unperturbed wave-functions. Since the matrix elements of $\Sigma a_i(\vec{l}_i\vec{s}_i)$ connect terms with $\Delta\wedge = 0, \pm 1$, $\Delta S = 0, \pm 1$ and $\Delta\Omega = 0$, all such terms have to be considered in taking the linear combinations. Thus, for example, for $\phi\,(^4\Pi_{\frac{1}{2}})$ can be written

$$\phi(^4\Pi_{\frac{1}{2}}) = C\phi^0(^1\Pi_{\frac{1}{2}}) + r_1\phi^0(^4\Sigma^+_{\frac{1}{2}}) + r_2\phi^0(^4\Sigma^-_{\frac{1}{2}}) + r_3\phi^0(^4\Sigma'_{\frac{1}{2}}) + r_4\phi^0(^4\Delta_{\frac{1}{2}}) + r_5\phi^0(^2\Sigma^+_{\frac{1}{2}}) + r_6\phi^0(^2\Sigma^-_{\frac{1}{2}}) + r_7\phi^0(^2\Pi_{\frac{1}{2}}) + \quad \ldots \quad (7)$$

where the unperturbed functions are denoted by ϕ^0 and the perturbed ones by ϕ, and the dots denote the other terms. The constants r are given by equations of the type

$$r_1 = \frac{\int \phi^{0*}(^1\Sigma^+_{\frac{1}{2}})\Sigma a_i(l_is_i)\phi^0(^1\Pi_{\frac{1}{2}})d\tau}{W_0(^1\Pi_{\frac{1}{2}}) - W_0(^4\Sigma^+_{\frac{1}{2}})} \quad \ldots \quad (8)$$

It can also be noted that for the first order of approximation C can be put equal to zero while second power terms in r can always be neglected wherever they occur. Using these perturbed wave-functions the matrix elements of H are given as linear combinations of the above unperturbed matrix elements H^0. Thus, for example, the following matrix elements can be written down from equation (7) and similar equations for $\phi\,(^2\Sigma_{\frac{1}{2}})$ and $\phi(^2\Pi_{\frac{1}{2}})$.

$$H(^2\Sigma_{\frac{1}{2}}, {}^4\Pi_{\frac{1}{2}}) = \bar{r}_1 H^0(^2\Sigma_{\frac{1}{2}}, {}^2\Pi_{\frac{1}{2}}) + \bar{r}H^0(^1\Sigma_{\frac{1}{2}}, {}^4\Pi_{\frac{1}{2}} + \bar{r}_3\bar{r}_4 H^0(^1\Pi_{\frac{1}{2}}, {}^4\Delta_{\frac{1}{2}}) + \quad \ldots \quad (9a)$$

$$H(^2\Sigma_{\frac{1}{2}}, {}^2\Pi_{\frac{1}{2}}) = H^0(^2\Sigma_{\frac{1}{2}}, {}^2\Pi_{\frac{1}{2}}) + \bar{r}_1 H^0(^2\Pi_{\frac{1}{2}}, {}^2\Delta_{\frac{1}{2}}) + \quad \ldots \quad (9b)$$

Here $\bar{r}_i$ are the approximate mean values of r_i. In equations of the type (9*a*) second order terms in r can be neglected while in equations of the type (9*b*) even first order terms in r can be neglected.

Once the matrix elements connecting the different states under consideration have been determined, the secular equation can be easily formed and the perturbed energies obtained by solving the same. The method of solving the secular equation is explained in detail for the perturbation case $^2\Sigma - {}^4\Pi$ discussed in this paper ; for the others the main results alone are reported.

CALCULATIONS AND RESULTS

The different states that have to be taken into consideration for the $^2\Sigma - {}^4\Pi$ perturbation are $^2\Sigma_{\frac{1}{2}}$, $^2\Sigma_{-\frac{1}{2}}$, $^4\Pi_{5/2}$, $^4\Pi_{3/2}$, $^4\Pi_{\frac{1}{2}}$, $^4\Pi_{-\frac{1}{2}}$, $^4\Pi'_{-5/2}$, $\Pi'_{-3/2}$, $\Pi'_{-\frac{1}{2}}$, $\Pi'_{\frac{1}{2}}$ where by Π and Π' are represented the states with $\wedge$ positive and negative

respectively. In this as well as in all other cases of perturbations the secular equation formed with wave-functions of this type can always be split up into two lower order equations under the transformation of these wave-functions into new functions ϕ_1' and ϕ_2' such that

$$\left.\begin{aligned}\phi_1'(\Lambda, \Sigma) &= 2^{-\frac{1}{2}}[\phi(\Lambda, \Sigma) + \phi(-\Lambda, -\Sigma)]\\ \phi_2'(\Lambda_2 \Sigma) &= 2^{-\frac{1}{2}}[\phi(\Lambda, \Sigma) - \phi(-\Lambda, -\Sigma)]\end{aligned}\right\} \quad \ldots \quad (10)$$

The new wave-functions ϕ_1' and ϕ_2' are identical with the Krönig symmetric and antisymmetric functions and possess the property that they go over into themselves (either with or without a change of sign) under reflection at the origin of all the coordinates concerned. In all the calculations below all the matrix elements will be given only after such a transformation has been effected. Numbering the new eigenfunctions from 1 to 10 with the first two representing the Σ states, the various matrix elements are obtained as follows :

$$W_1^0 = B_\Sigma(J+\tfrac{3}{2})(J+\tfrac{1}{2}) \qquad W_2^0 = B(J+\tfrac{1}{2})(J-\tfrac{1}{2})$$

$$W_3^0 = W_7^0 = h\nu(\Sigma, \Pi) + B\pi[J(J+1) - \tfrac{1}{4}^2] + \tfrac{3}{2}A \qquad W_4^0 = W_8^0 = h\nu(\Sigma, \Pi) + B\pi[J(J+1) + \tfrac{5}{4}] + \tfrac{1}{2}A$$

$$W_5^0 = W_9^0 = h\nu(\Sigma, \Pi) + B\pi[J(J+1) + \tfrac{1}{4}^3] - \tfrac{1}{2}A \qquad W_6^0 = W_{10}^0 = h\nu(\Sigma, \Pi) + B\pi[J(J+1) + \tfrac{5}{4}] - \tfrac{3}{2}A$$

$$H_{34}^0 = H_{78}^0 = B\pi\sqrt{(J+\tfrac{5}{2})(J-\tfrac{3}{2})} \qquad H_{45}^0 = H_{89}^0 = 2B\pi\sqrt{(J+\tfrac{3}{2})(J-\tfrac{1}{2})}$$

$$H_{56}^0 = H_{9,10}^0 = \sqrt{3}\,B\pi(J+\tfrac{1}{2})$$

$$H_{14}^0 = H_{28}^0 = [1 \pm (-1)^\Sigma]\phi_1\sqrt{(J+\tfrac{3}{2})(J-\tfrac{1}{2})} \qquad -H_{16}^0 = H_{2,10}^0 = [\pm 1 + (-1)^\Sigma]\mu_2$$

$$H_{18}^0 = H_{24}^0 \qquad -H_{1,10}^0 = H_{26}^0$$

$$H_{15}^0 = [1 \pm (-1)^\Sigma]\{\mu_1 + \phi_2(J+\tfrac{1}{2})\} \qquad H_{29}^0 = [1 \pm (-1)^\Sigma]\{\mu_1 - \phi_2(J+\tfrac{1}{2})\}$$

$$H_{25}^0 \qquad H_{19}^0$$

$$H_{12}^0 = 0 \qquad \text{and} \qquad H_{ik}^0 = H_{ki}^{0*}\ H_{kl}^{0*}.$$

here ϕ_1, ϕ_2, μ_1 and μ_2 are constants independant of J and depending only on the electronic structure of the molecule.

With these matrix elements the 10th order secular determinant breaks up into two fifth order determinants, each of which can be separately equated to zero. These determinants are identical in all respects except that one of these contains only positive terms while the other contains only the negative terms for each J. Hence only one of these is solved here since exactly similar equations apply to the other case also.

The form of this secular determinant is

$$\begin{array}{|cc|cccc|}
{}^2\Sigma & W_1^0 - W & 0 & H_{14}^0 & H_{15}^0 & H_{16}^0 \\
\hline
 & 0 & W_3^0 - W & H_{34}^0 & 0 & 0 \\
{}^4\Pi & H_{41}^0 & H_{43}^0 & W_4^0 - W & H_{45}^0 & 0 \\
 & H_{51}^0 & 0 & H_{54}^0 & W_5^0 - W & H_{56}^0 \\
 & H_{61}^0 & 0 & 0 & H_{65}^0 & W_6^0 - W
\end{array} \qquad (12)$$

Now we transform this matrix with a unitary matrix S so that in the transformed matrix $(H = S^{-1}H^0S)$ the ${}^4\Pi$ portion becomes diagonal. The eigenvalues of the ${}^4\Pi$ state in the general intermediate case of coupling are given by Brandt (1936). If these are denoted by W'_3, W'_4, W'_5, and W'_6 then the elements of S are given by

$$\left.\begin{aligned}
S_{ik} &= [s_{3k}^2 + s_{4k}^2 + s_{5k}^2 + s_{6k}^2]^{-1/2} s_{ik} \qquad (i, k = 3, 4, 5, 6) \\
s_{3k} &= [3(J-\tfrac{3}{2})(J+\tfrac{5}{2})]^{1/2}[(W'_5 - W_k)(W'_6 - W_k) - 3(J+\tfrac{1}{2})^2] \\
s_{4k} &= -(W'_3 - W_k)[(W'_5 - W_k)(W'_6 - W_k) - 3(J+\tfrac{1}{2})^2] \\
s_{5k} &= 2[(J-\tfrac{1}{2})(J+\tfrac{3}{2})]^{1/2}(W'_3 - W_k)(W'_6 - W_k) \\
s_{6k} &= -2[3(J-\tfrac{1}{2})(J+\tfrac{3}{2})]^{1/2}(J+\tfrac{1}{2})(W'_3 - W_k)
\end{aligned}\right\} \qquad (13)$$

Further $S_{11} = 1$ and the remaining elements of S are zero. If the ${}^4\Pi$ state belongs to case (*a*) the S matrix becomes a unit matrix, while if it belongs completely to case (*b*) coupling the S matrix is given by

$$\begin{array}{cccc}
\left(\frac{2J-3}{16J}\right)^{\frac{1}{2}} & \left(\frac{3(2J-3)}{16J}\right)^{\frac{1}{2}} & \left(\frac{3(2J+3)(2J-3)}{16J(2J-1)}\right)^{\frac{1}{2}} & \left(\frac{(2J+5)(2J+3)}{16J(2J-1)}\right)^{\frac{1}{2}} \\
\left(\frac{3(J+1)}{J+1}\right)^{\frac{1}{2}} & \left(\frac{(2J+5)^2}{16(J+1)(2J+1)}\right)^{\frac{1}{2}} & \left(\frac{(2J+3)(2J-7)^2}{16(J+1)(2J+1)(2J-1)}\right)^{\frac{1}{2}} & \left(\frac{3(2J+5)(2J+3)(2J-3)}{16(J+1)(2J+1)(2J-1)}\right)^{\frac{1}{2}} \\
\left(\frac{3(2J+1)}{16J}\right)^{\frac{1}{2}} & \left(\frac{(2J-3)^2}{16(2J+1)J}\right)^{\frac{1}{2}} & \left(\frac{(2J+9)^2(2J-1)}{16(2J+3)(2J+1)J}\right)^{\frac{1}{2}} & \left(\frac{3(2J+5)(2J-1)(2J-3)}{16(2J+3)(2J+1)J}\right)^{\frac{1}{2}} \\
\left(\frac{2J+5}{16(J+1)}\right)^{\frac{1}{2}} & \left(\frac{3(2J+5)}{16(J+1)}\right)^{\frac{1}{2}} & \left(\frac{3(2J+5)(2J-1)}{16(2J+3)(J+1)}\right)^{\frac{1}{2}} & \left(\frac{(2J-1)(2J-3)}{16(2J+3)(J+1)}\right)^{\frac{1}{2}}
\end{array} \qquad (14)$$

After the transformation the secular equation can be represented by

$$\begin{array}{|cccc|}
W_1 - W & H_{13} & H_{14} & H_{15} & H_{16} \\
H_{31} & W_3 - W & 0 & 0 & 0 \\
H_{41} & 0 & W_4 - W & 0 & 0 \\
H_{51} & 0 & 0 & W_5 - W & 0 \\
H_{61} & 0 & 0 & 0 & W_6 - W
\end{array} = 0 \qquad (15)$$

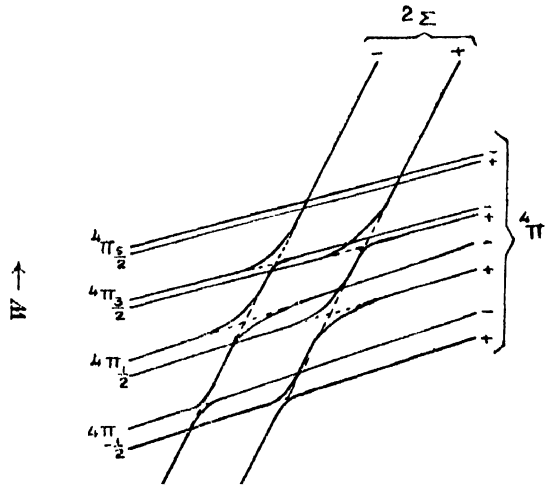
where $H_{1k} = S^*_{k4}H^0_{14} + S^*_{k5}H^0_{15} + S^*_{k6}H^0_{16}$, and $H_{kl} = H^*_{lk}$

Now it can be shown that at the crossing point of two levels (say, the levels i and k) the effect of all matrix elements except those directly connecting these levels (H_{ik} and H_{ki}) is negligible. Hence for the calculation of the perturbed energy values in the immediate neighbourhood of the crossing point of two levels it will be sufficient to diagonalise just this part of the secular determinant. Thus we have for the perturbed energy W'_i and W'_k

$$\left.\begin{matrix} W'_i \\ W'_k \end{matrix}\right\} = W_i + W_k \pm \sqrt{\left(\frac{W_i - W_k}{2}\right)^2 + H_i} \qquad (16)$$

For the present purpose $i=1$ and $k=3, 4, 5, 6$.

On solving the second determinantal equation the same final equation will be obtained except that here $i=2$ and $k=7, 8, 9, 10$. Thus we see that one set of the Λ components of the $^4\Pi$ state are perturbed only by one component of the $^2\Sigma$ state, while the other set of the $^4\Pi$ components are perterbed by the remaining component of the $^2\Sigma$ state.



$J(J+1)\rightarrow$

Fig.1

A diagrammatic representation of this case is given in figure 1, where the energy levels W are plotted against $J(J+1)$. The figure is not drawn to scale but the relative magnitudes of the various perturbations are qualitatively correct. The thin lines represent the unperturbed levels while the thick lines represent the perturbed levels.

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